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PILOT-PLANT STUDIES OF AN ANHYDROUS
MELT GRANULATION PROCESS
FOR AMMONIUM PHOSPHATE-BASED FERTILISERS

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The Tennessee Valley Authority has developed on pilot-plant scale a simple melt-type granulation process for the production of ammonium phosphate-based fertilisers from merchant-grade wet-process phosphoric acid. The process is an outgrowth of TVA's work on the direct process for production of ammonium polyphosphate (1). In practice, this process consists of operating the direct-process reaction system in the temperature range required to produce an anhydrous ammonium phosphate melt of about 12-57-0 grade with about 20 to 30% of the P_2O_5 in polyphosphate form. With the polyphosphate content in this range, the melt can be granulated without difficulty in a pug mill. The polyphosphate content is high enough to provide a fluid melt with good flow characteristics but is low enough to crystallize readily and granulate with moderate rates of recycle. Urea and potassium chloride can be added to make products of such grades as 21-42-0, 28-28-0, and 19-19-19 or ammonium nitrate for grades such as 25-25-0 and 17-17-17. The chief advantage of the process is that only anhydrous materials are fed to the pug mill, thus eliminating the need for a dryer. Also, the storage properties of the products containing urea are distinctly better than similar products made by conventional processes.

In the direct process, heat from the reaction of ammonia with merchant-grade acid is utilised to evaporate all of the free water and a portion of the combined water. Evaporation of the combined water results in the formation of polyphosphates. By this means, melts containing 50% or more of the P_2O_5 in the polyphosphate form can be produced. Such melts are excellent materials for use in preparation of fluid fertilisers because of the high water solubility of the phosphates in the ammonium phosphate - ammonium polyphosphate system. Attempts to granulate the 50% polyphosphate melt were

disappointing ; granulation of this material required about 16 pounds of recycle per pound of product and excessive power to control plasticity in the pug mill because the melt did not crystallize readily. Subsequent pilot-plant studies have shown that granulation characteristics of the melt improve markedly when polyphosphate content is limited to 20 to 30% by lowering the reactor temperature from 245° (470°) to about 205° to 220° C (400°-430° F). The low-polyphosphate melt crystallizes readily and can be granulated easily at recycle ratios of 4:1 or less.

DESCRIPTION OF THE PILOT PLANT

The pilot plant consisted of a reaction system for preparation of the ammonium phosphate melt ; a granulation section including a pug mill and cooling, screening, and crushing equipment ; and facilities for adding urea and potash. A flow diagram of the entire process is shown in Figure 1. The pilot plant was operated at rates of 500 to 1500 pounds per hour of granular product.

Details of the melt preparation system are shown in Figure 2. In this countercurrent reaction system, the wet-process feed acid initially was utilized in an 8-inch-diameter spray scrubber to remove unreacted ammonia from the reactor off-gas. Partially neutralized acid was pumped at a controlled rate from the scrubber to a 4-inch pipe tee reactor where all of the anhydrous ammonia was fed. The partially neutralized acid and ammonia reacted to form an ammonium polyphosphate melt. Because of the very short retention in the tee reactor, there was essentially no reversion of phosphate to a citrate-insoluble form. The melt from the tee reactor discharged in an extremely foamy state through about 3 feet of 1½-inch pipe into a vapor disengager. The disengager, shown in Figure 3, was a 24-inch-long horizontal tube 6½ inches in diameter containing a rotor with two helical blades. The rotor spread the melt against the wall of the vessel and thereby provided a large surface area for separation of the steam and unreacted ammonia from the melt. The pitch and rotation of the blades were such that the melt was conveyed to the discharge end of the disengager. Significantly, the shearing action of the blades transformed the foamy melt into a free-flowing fluid. A blower moved steam and unreacted ammonia from the vapor disengager through the spray scrubber. Normally, a negative pressure of about 1 inch of water was maintained at the scrubber outlet. The disengager was placed directly above the pug mill so that the melt could fall freely into this granulator. A photograph of the disengager and pug mill is shown in Figure 4. The spray scrubber, disengager, and piping were made of Type 316L stainless steel.

The pug mill had 19 cubic feet of effective working volume in a 7-foot-long bed which was 22 inches wide. Its 4-inch-diameter shafts were equipped with 5 $\frac{1}{2}$ -inch-long mixing paddles and were driven at 43 rpm by a 25-horsepower motor. The bed sloped slightly toward the discharge end, and an adjustable gate was used to control the bed depth. Material from the pug mill was cooled with about 600 cfm of ambient air in a 30-inch-diameter rotary cooler 21 feet long. The cooler turned at 10 rpm. The cooled material was screened at minus 6 plus 9 mesh for the product. A chain mill crushed the oversize material in a closed circuit with an undersize screen so that no crushed material was in the product, and the recycle was all minus 9 mesh.

Urea was fed either as concentrated solution sprayed into the pug mill or fed as prills onto the recycle return belt. A two-stage, steam-heated urea melter produced the solution from commercial prills at a concentration of about 99% and a temperature of 140° C (280° F). When NPK grades were produced, the potassium chloride was fed onto the recycle belt as standard-size material (60% K₂O).

MELT PRODUCTION

The low-polyphosphate melt was produced from typical Florida merchant-grade wet-process acid made from uncalcined rock. The analysis of the acid used in most of the work is shown in the table below.

Chemical composition, % by wt.

<u>P₂O₅</u>	<u>Fe₂O₃</u>	<u>Al₂O₃</u>	<u>SO₃</u>	<u>F</u>	<u>Mg</u>	<u>Water-insoluble solids</u>
51.1	1.5	1.2	3.2	0.8	0.3	5.1

Typical operating conditions for the reaction system and analyses of ammonium phosphate melts for tests at a production rate of 500 pounds per hour are shown in Table I.

Since the acid contained only 50 to 51% P₂O₅, it was necessary to preheat it to 60° (140°) to 132° C (270° F) to maintain reaction temperatures high enough to convert the desired proportion of P₂O₅ to polyphosphate form. No preheat should be required for acid if it were at a concentration of 53 to 54%. The flow of ammonia to the tee reactor was closely controlled so that enough unreacted ammonia passed to the scrubber to maintain the pH of the acid there at about 1.8 (10% aqueous solution). At this pH the acid contained about 2 pounds of ammonia per unit of P₂O₅, which is in a range of high solubility of the ammonium phosphate as shown in Figure 5.

Conversion of orthophosphate to polyphosphate in the tee reactor and vapor disengager usually ranged from 18 to 33% ; for 19-19-19 grade, increasing the polyphosphate content to about 40% resulted in better incorporation of the potash. The grade of the ammonium phosphate melt was 13-55-0 when the tee reactor temperature was 210° C (410° F) ; less nitrogen was fixed at higher temperatures, resulting in a 12-57-0 grade at 227° C (440° F). The P₂O₅ in the melt was 98 to 99% water soluble and 99 to 100% citrate soluble. The water solubility is significantly higher than obtained with the same type of acid in orthophosphate products.

The ammonia loss and rate of fluorine evolution from the process were evaluated. The amount of ammonia lost from the spray scrubber was too small to be detected in gas-sampling tests. Gas samples analysed for fluorine indicated that 2.4% of the fluorine in the feed acid was evolved. In another test the F:P₂O₅ ratio in the product was compared with that of the feed acid ; this comparison indicated that about 7% of the fluorine in the acid had been evolved.

Tests with corrosion specimens mounted in the pilot-plant equipment showed that Type 316 stainless steel corroded at high rates, about 100 mils per year in the scrubber and as high as 500 mils per year when exposed to the hot melt. These tests indicated that Hastelloy G or Alloy 20 would be satisfactory for the scrubber, and Hastelloy C could be used for the disengager. Hastelloy C should be satisfactory for the tee reactor. Since the components in the reaction system are comparatively small, use of corrosion-resistant alloys should not be unduly expensive.

GRANULATION

The principal objective of the granulation studies was to determine the best conditions for operation of the pug mill. The effects of recycle ratio and the polyphosphate content of the melt were investigated, and the pug mill slope and bed depth were varied to obtain the best operation. For each grade of product, a range of polyphosphate conversion in the melt was established which provided sufficient plasticity for good granulation but did not require excessive amounts of recycle. The pug mill gave the best mixing of melt and recycle when nearly level, so that the bed was full to about the top of the paddles. In a few tests, the pug mill was discharged to a rotary drum granulator in an effort to improve granulation efficiency. Use of the drum did not affect the particle-size distribution, but the rolling action improved the appearance of the granules. The test data shown in Table II are typical of operation at a recycle ratio high enough to avoid excessive plasticity and stickiness in the pug mill and yet low enough to obtain

adequate granulation for providing the necessary preparation of product. The mechanical working of the melt in the pug mill is beneficial in promoting crystallization and resultant granulation. Also, a pug mill is particularly suited for specific placement of the two melts to avoid contact at high temperature. However, rotary drum or other types of granulators probably would be adaptable to this process.

The 12-57-0 grade was the basis for all the other grades and was also the simplest to granulate, merely involving mixing melt with recycle. In the pilot plant, 500 pounds per hour of melt was granulated at a recycle ratio of 3.8:1, giving a temperature of 99° C (210° F) in the pug mill. The proportion of oversize material was high (34%), but it was easily crushed and handled. The optimum polyphosphate level for granulation of this product was 25 to 30% of the total P₂O₅.

The 21-42-0 grade product was produced at a rate of 1,000 pounds per hour using 750 pounds of ammonium phosphate melt and 250 pounds of concentrated (99%) urea solution per hour. When using urea in the solution form, it was found necessary to spray the solution onto the recycle at the feed end of the pug mill followed by the addition of the ammonium phosphate melt at a point in the mill after the solution had crystallized. This procedure ensured incorporation of the urea into the granules by overcoating with melt and prevented hydrolysis of urea by the hot ammonium polyphosphate melt. Hydrolysis is undesirable because it results in loss of ammonia and foaming and stickiness in the pug mill. Also, this procedure of overcoating the urea with ammonium phosphate melt minimized dusting of urea from the product. The sequential placement of recycle, followed by urea melt, and then by the ammonium phosphate melt in the pug mill was very important. Best pug mill operation was obtained at a recycle ratio of about 3 and a temperature of 89° C (192° F). The product grade was 20.8-42.3-0 and analyses showed that no biuret was formed during granulation.

Production of the 28-28-0 grade at a rate of $\frac{1}{2}$ short ton per hour required 500 pounds each of melt and urea. Operation with urea solution was similar to that for 21-42-0 grade except that a higher recycle ratio, about 4:1, was required. The temperature in the pug mill was 86° C (186° F). Operation with solid (prilled) urea was satisfactory and easily controlled using melt with 27% of its P₂O₅ as polyphosphate, but some uncoated urea prills could be seen in the product. This condition probably could be prevented by using prills of smaller size such as microprills. Only about 2 pounds of recycle was required per pound of product, and the temperature in the pug mill was 79° C (175° F) when prilled urea was used.

The 19-19-19 grade was granulated at a rate of about 1,500 pounds per hour. Melt and urea solution were fed to the pug mill as in 28-28-0 production, and standard size potassium chloride was fed along with the recycle. Incorporation of the potash was somewhat difficult with the limited liquid phase provided by the two anhydrous melts. Increasing the polyphosphate content to 33% gave additional plasticity for incorporating the potash. A recycle ratio of 3:1 and pug mill temperature of 80° C (176° F) gave the best operation. In a later test, a further increase in polyphosphate content of the melt to about 40% was beneficial in granulation of the 19-19-19 grade.

The extent to which impurities in wet-process acid affect crystallization of the ammonium phosphate melt is not known. With acids of differing impurity distribution and content, the polyphosphate ranges required for granulation likely will differ. In the pilot-plant pug mill the degree of plasticity needed for good granulation also favored the formation of amounts of oversize material that usually were about equal to the amount of product size. In a large plant the proportion of oversize should be substantially less, however, because larger pug mills give better mixing due to the greater tip speed of the paddles. In the TVA demonstration-scale plant for production of 15-62-0 ammonium polyphosphate from electric-furnace superphosphoric acid, the proportion of oversize is about one-third of the product-size material (2).

STORAGE PROPERTIES

All the product grades had good storage and handling properties. The products that contained urea appeared to store much better in bulk than similar products in which the phosphate was entirely orthophosphate. Moisture absorption was limited to a very light crust on the surface, and the piles were free from lumps or caking. The polyphosphate content apparently acts as a "built-in" conditioner for moisture protection.

Bag-storage tests were made using 50-pound bags loaded under pressure equivalent to a stack 20 bags high and stored in an unheated, well-ventilated building. Unconditioned 12-57-0 grade (-6 +9 mesh) was not caked when examined after 7 months' storage in bags of 4-ply paper with two asphalt-laminated plies. The grades containing urea were satisfactory in this type bag for 1 month without conditioner, but on further storage the material absorbed excessive moisture and caked. However, these grades were in satisfactory condition after 9 months when the 4-ply bag was sealed in a 4-mil polyethylene overbag. Bags with polyethylene inner liners should be satisfactory also. Addition of 2% conditioning

dust, either diatomaceous earth or kaolin, prevented caking of the urea grades during 9 months in the 4-ply bag.

The critical relative humidity was 60 to 65% for the 12-57-0 grade and 50 to 55% for all the grades containing urea, compared with about 75% for commercial diammonium phosphate. For all the grades, however, resistance of the unconditioned bulk material to penetration by moisture from humid atmosphere was about the same as for commercial diammonium phosphate. No difficulties in handling the bulk materials are therefore expected. Bulk density of the products ranged from 46.4 to 49.3 pounds per cubic foot.

CONCLUSIONS

The process for the granulation of low-polyphosphate melt is technically proved, operationally simple, and should be adaptable commercially as an alternative to present diammonium phosphate and triple superphosphate process. It seems to be particularly well suited to preparation of urea - ammonium phosphate-type fertilisers. The 12-57-0 grade product fixes less ammonia than diammonium phosphate but is more concentrated in P_2O_5 than either diammonium phosphate or triple superphosphate. The reaction system is simple, dependable, and easy to control; corrosion-resistant materials of construction are required. However, eliminating the dryer from a granulation plant saves in both investment and operating costs as well as decreasing dust and fume problems. A process without a dryer is especially important in the production of mixed fertilisers containing urea or ammonium nitrate since drying is difficult and long retention time and low-temperature air must be used (3). Only limited tests have been made using ammonium nitrate to provide supplemental nitrogen, but additional work is planned and will be reported at the technical session of International Superphosphate and Compound Manufacturers' Association Limited.

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LITERATURE CITED

1. Meline, R.S., Davis, C.H., and Lee, R.G., Farm Chem.
2. Kelso, T.M., Stumpe, J.J., and Williamson, P.C., Com. Fertiliser 116, No. 3, 10-16 (Mar. 1968).
3. Meline, R.S., Hicks, G.C., Kelso, T.M., and Norton, M.M., Ind. Eng. Chem. 7, 124-133 (Jan. 1968).

Table I - OPERATION OF REACTION SYSTEM

Test No.	201	207	209	253
Product (melt) rate, lb./hr.	500	500	500	500
Feed acid - Temp., °F	270	140	270	272
- P ₂ O ₅ , %	50.1	50.7	51.0	53.4
Scrubber - Temp., °F	281	263	290	280
- pH (10% solution)	1.8	1.9	1.8	1.7
Temp., °F - Ammonia	300	260	320	80
- Tee reactor	440	410	432	457
Ammonium phosphate melt				
- pH (10% solution)	4.5	5.2	4.7	4.2
- Per cent by wt. N	12.5	13.4	13.0	12.3
P ₂ O ₅	57.2	55.4	56.6	58.6
- Per cent of total P ₂ O ₅				
Polyphosphate	27	18	33	40
Water soluble	99	98	98	-
Available	99.6	100	99.8	-
- Degree of ammoniation, lb. NH ₃ /unit of P ₂ O ₅	5.3	5.9	5.6	5.1

Table II - PILOT-PLANT GRANULATION OF AMMONIUM PHOSPHATE MELT

	Product grade					
	12-57-0	21-42-0	28-28-0		19-19-19	
Test No.	201-2	208	207	122	209-2	253
Test length, hr.	4.7	2.7	5.0	4.8	4.5	3.5
Product rate, lb./hr.	500	1000	1000	1350	1480	1480
Feed acid						
P ₂ O ₅ , %	50.1	50.7	50.7	51.8	51.0	53.4
Temp., °F	270	115	140	100	270	272
Ammonium phosphate melt						
Rate, lb./hr.	500	750	500	675	500	500
Temp., °F	440	405	410	390	432	457
Urea rate, lb./hr.	-	250 ^a	500 ^a	675 ^b	500	500
Potash ^c rate, lb./hr.	-	-	-	-	480	480
Recycle						
Ratio	3.8	3.2	3.9	2.3	3.0	3.1
Rate, lb./hr.	1900	3200	3900	3100	4400	4560
Temp., °F	92	102	104	-	122	126
Screen analysis, % by wt.						
+6 mesh	0	1	2	-	2	-
-6 +10 mesh	6	25	27	-	24	-
-10 mesh	94	74	71	-	74	-
Pug mill slope, in./ft.	1.0	0.2	0.2	0	0.2	0
Pug mill product						
Temp., °F	210	192	186	175	176	168
Screen analysis, % by wt.						
+6 mesh	34	28	29	24	26	19
-6 +10 mesh	23	28	31	27	30	21
-10 mesh	43	44	40	49	44	60
Analysis of screened product (-6 +9 mesh)						
Per cent by wt. N	12.3	20.8	28.1	27.4	20.1	20.5
P ₂ O ₅	56.8	42.3	30.6	30.4	19.4	19.7
K ₂ O	-	-	-	-	19.1	17.8
H ₂ O	0.8	0.7	0.6	0.8	0.5	1.0
Per cent of total P ₂ O ₅						
Polyphosphate	25	17	18	27	34	38
Water soluble	99	98	98	-	98	93
Available	99.4	100	100	100	100	100

^a Approximately 99% solution at about 280° F.

^b Prilled, unconditioned urea fed at 675 lb./hr. with the recycle.

^c Standard muriate of potash (60% K₂O).

LIST OF FIGURES

1. Flow Diagram for Direct Production of Low-Polyphosphate Granular Products
2. Flow Diagram of Reaction System for Direct Production of Ammonium Polyphosphate
3. Vapor Disengager
4. Equipment Arrangement for Production of Granular Products
5. Effect of $\text{NH}_3:\text{H}_3\text{PO}_4$ Mole Ratio on Solubility of Ammonium Phosphate at 167°F

DISCUSSION

Mr. R.D. YOUNG (Tennessee Valley Authority) : Slide 1 shows the reaction system as developed in pilot-plant work over a rather long period of experimentation. Basically it utilizes the heat of reaction of ammonia and phosphoric acid to remove water and form the anhydrous melt with part of the phosphate in polyphosphate form (the system as shown in Figure 2 of the paper was described briefly).

- Melts covering wide range of polyphosphate content can be produced.
- Polyphosphate content of the melt was varied by strength and degree of preheat of feed acid ; temperature in the tee reactor (200-240° C) controls polyphosphate content.
- Melts of lower polyphosphate content are better for granulation ; those of higher polyphosphate content better for liquids.

The work on use of the melts of lower polyphosphate content in granulation together with supplemental materials actually was a side effort in our main studies of preparing polyphosphates directly from wet-process acid. The melts with about 50% of the P₂O₅ as polyphosphate are very difficult to granulate because of slow crystallization. However, we found that lowering the polyphosphate content to the range of 15 to 35% gave melts that granulated readily in a pug mill or blunger. Melts with polyphosphate content lower than about 10% did not have good fluid properties in the reaction system and crystallized too rapidly for good granulation.

Slide 2 shows typical reaction conditions for a melt of about 25% polyphosphate content that is suitable for granulation.

Melt production rate, lb/hr	500
Acid used :	
P ₂ O ₅ , %	53
Temperature	27° C (80° F) - no pre-heating
Tee reactor temperature	213° C (415° F)
Melt analysis, % by weight :	
N	12.4
P ₂ O ₅	57.3

Percent of total P ₂ O ₅ as :	
Polyphosphate	25
Water soluble	99
Neutral citrate soluble	100

Slide 3 (Fig. 1 of manuscript) shows the pilot-plant system for granulation (the system for operation with urea and with ammonium nitrate were described and differences were explained. The advantage of higher polyphosphate for potash grades was explained).

We did not have much experience with ammonium nitrate as the supplemental material when the paper was submitted. Since that time we have developed suitable techniques for its use. The main difference is that the ammonium nitrate solution and ammonium phosphate melt can be premixed before feeding to the pug mill whilst the urea cannot.

Slide 4 shows main operating conditions for products containing urea and for 25-25-0 containing ammonium nitrate.

<u>Grade</u>	28-28-0	19-19-19	25-25-0
Rate, lb/hr :			
Phosphate melt	500	500	500
Urea (99% soln.)	500	500	-
Ammonium nitrate (97% soln.)	-	-	670
Potassium chloride	-	480	-
Recycle ratio	3.9	3.0	3.6
Pug mill product temperature	84° C (183° F)	80° C (176° F)	93° C (200° F)
Analysis of product, % by weight :			
N	28.5	20.1	24.8
P ₂ O ₅	28.5	19.4	24.8
K ₂ O	-	19.1	-
Percent of total P ₂ O ₅ :			
Polyphosphate	25	38	35
Water soluble	99	98	98
Citrate soluble	100	100	100

In concluding my remarks I would like to stress some of the primary advantages of this process.

- No drying step is required.
- Improved physical properties of products are obtained.

- Higher water solubility of phosphate in products.
- Polyphosphate content could be beneficial.

Mr. W.H. COATES (Albright and Wilson) : The authors have presented a most interesting paper describing the manufacture of ammonium phosphate-based fertilisers based on merchant grade wet phosphoric acid using a melt technique. This is an important development of work which has been carried out over the past few years by T.V.A. in which thermal and superphosphoric acids were used. It offers a simple method of producing high grade fertilisers which could very well lead both to lower capital costs and particularly to lower operational costs. It is interesting to note that they have produced a product containing almost 60% P_2O_5 , all substantially water soluble, from phosphoric acid solutions which have, in fact, a lower P_2O_5 content than the end product, and this process therefore has some considerable significance and considerable potential in opening up still further the possibilities of international transportation of P_2O_5 from those areas in the world where it can be produced most cheaply.

As in many other melt processes, advantage is taken of the exothermic energy available when phosphoric acid is neutralised by ammonia to remove the moisture and in this way eliminate the need for external drying operations which is a very important aspect from the point of view of economy and possibly also from the point of view of elimination of the problems and possible hazards of decomposition which could occur by the application of external heat. It also makes concentration of acid to super acid unnecessary. It would appear that the products produced from the limited scale experiments which have been carried out have excellent storage properties and it is most important that further experimental work is carried out to confirm this. The plant runs reported in the paper are of limited duration and it is clearly most desirable to extend this operation to confirm the results which have already been obtained. As a matter of general interest, have these products better storage properties than those prepared from thermal acid ?

The paper raises one or two rather interesting technical questions which will have an impact on this process and perhaps other melt processes, too. In particular, there is a reference to the significance of impurities in the phosphoric acid insofar as such impurities can affect crystallization. The authors say that they are not clear which of the impurities is important in effecting this degree of control. We, too, have found in our operations in a melt process that impurities in phosphoric acid, as well as temperature, are

extremely important in the formation of polyphosphate and in particular it would appear that the insoluble calcium sulphate content could be quite important. Surprisingly, also, we have found that the presence of small amounts of organic matter can have significance in the formation of polyphosphate and the crystallization temperature of the melt. Can the authors of the paper make any comment about the possible effects of organic matter and offer any explanation for these somewhat surprising effects ?

By using a higher concentration of phosphoric acid it is claimed, and apparently demonstrated, that it is not necessary to provide any additional heat in the system. It is not clear under these circumstances how the temperature of the scrubbing tower is controlled. This presumably will be at a sufficiently high temperature to prevent condensation of the water which is driven off from the system. Would the authors please explain this situation in more detail ?

The reference to the production of NPK fertiliser, in particular grade 19-19-19, is most interesting. It would appear that there is some difficulty in incorporating KCl into the melt because of the limited amount of plasticity available from the ammonium phosphate/urea melt. It would be of interest to have the authors' opinion on the possibility of producing a high grade low nitrogen, high P, high K formulation, perhaps of a 1-5-5 type. Is it possible that by modifying the method of addition of KCl to the ammonium phosphate polyphosphate melt, increased amounts of KCl could be incorporated ? The manner of adding the potash to the system is apparently a very simple one and this could be improved upon. For instance, by introducing between the vapour disengager and the pug mill a vessel which would give more intimate mixing, would it not be possible to introduce a higher amount of KCl ? Also, grinding and heating the potash may help larger amounts to be incorporated. I mention this matter because particularly in European conditions, whilst there are satisfactory melt processes developed to produce compounds containing high percentages of N (chiefly based on ammonium nitrate), similar processes for the production of compounds containing high amounts of K have not been satisfactorily developed.

In conclusion, I would like to say again this is a most interesting development and one which could have a considerable effect on the costs of producing high grade fertilisers, and particularly if it could be extended to produce fertilisers incorporating large amounts of potash it could have even wider possibilities of development than the authors currently envisage. The paper is full of "meat" and I am sure this will create a lot of interest. I am also sure there will be many questions raised about the paper and I look forward to a stimulating discussion.

Mr. YOUNG : I feel Mr. COATES did stress and reinforce some of the advantages we saw for this process, and perhaps pointed out some other things that we will look into to increase the versatility. Some of the questions concerned the storage properties. We have evaluated these products over a long period of time and are continuing the storage tests. We do find the products to have very good physical properties if plastic plyed bags are used ; we have not had to use a conditioner on most grades. We will continue to evaluate the storage properties.

He mentioned the short duration of most of our pilot-plant runs. Since the paper was submitted we have operated for longer periods. We have run for periods around the clock, and we found in extended operation that the granulation was stabilised and improved with the length of duration of the run. We have encountered a problem due to build up and accumulation of crystal material between the tee reactor and the disengager. We are studying this problem. It is related to the impurities in the acid and we expect to find either mechanical or chemical means to get around it. We are quite sure it is related to the amount of impurities in the acid.

Mr. COATES asked a specific question on whether the storage properties are better with this system than in the products made with thermal acid. Yes they are, and we find that any products made with wet acid have better storage properties than similar products made with furnace acid. The impurities in the wet acid that are so troublesome in manufacture, handling and storage always prove beneficial when they are finally in the finished product. We think that impurities such as iron and aluminium act as a built-in conditioner perhaps to take up moisture and improve storage. In this polyphosphate product we find that the products are still better than those in the ortho system. We think this is related to the polyphosphate and perhaps, as was mentioned yesterday in a paper, due to the coating of the polyphosphate material on the surface of the granules.

Mr. COATES mentioned their experience with impurities in their factory, impurities on polyphosphate formation and rate of crystallization. His comments concerning calcium sulphate are particularly interesting and I would like to talk to him later about this. We find that the organics in acid that is made from uncalcined rock certainly have an effect on the mechanical operation. The foaming is much more pronounced and the disengager is much more necessary with acid made from raw rock. It does contain considerable organic matter. In our limited experience with acid made from calcined rock, we have found that we operate the disengager blade at much lower speed because there is not so much foaming and the action of

the blade can increase the rate of crystallization of the polyphosphate. So it is necessary to vary operating conditions depending on the impurities in the acid that is used.

He asked a question concerning temperature control in the scrubber when we operate with acid of 53% P_2O_5 or higher which is not pre-heated. We have found that, due to the heat of reaction, a substantial proportion of the ammoniation actually takes place in the scrubber. Our main control point is to control the pH of the acid in the scrubber at very near 1.8. This ensures that we are in a high solubility range and a mole ratio of about 0.4 in the acid. With this acid, we have not had temperatures lower than $130^{\circ}C$ in the scrubber, which is high enough to ensure that the water does not condense in the scrubber. The other main control point, other than the 1.8 pH in the scrubber, is temperature in the tee reactor. This temperature establishes the polyphosphate content and is a very main control point. This is controlled mainly by the strength and degree of pre-heat of the phosphoric acid.

Mr. COATES' comments concerning the addition of potash to the system are particularly interesting. We found it desirable to add the potash separately in the case of the urea grades because we want to apply the polyphosphate melt as the final coating on the material. If the urea solution is fed last it foams on the surface of the granules and we found quite a dusty situation when the fine particles of urea flaked off the granules. If the polyphosphate melt is added last, it forms an overcoating and prevents the dusting of urea from the granules. With ammonium nitrate, as I mentioned in the slide, we found advantages in pre-mixing with the melt to give better incorporation. In this case, perhaps we could add at least part of the potash in a pre-mixing vessel, as Mr. COATES suggested, and get still a greater incorporation of KCl. This also should be possible for grades such as the 1-5-5 that you mention. We have not tested that grade but I thoroughly appreciate your pointing out the significance of it and we will obtain some experience with grades of that type. There again, I think it should be possible to mix in at least part of the potash with the material before we go to the pug mill.

Mr. NOIRBENT (Kaltenbach, France) : My first question concerns safety. The manufacture of NPK from polyphosphate mixed with ammonium nitrate and chlorides (potassium chloride) has been referred to. I should like to know if T.V.A. has carried out "cigar-burning" trials and has any idea of the greater or lesser risk of "cigar-burning" in the case of NPK made with polyphosphates.

My second question concerns the pug mill technique. Since there is a melted mass, why has the prilling technique not been adopted ?

My third question concerns the equipment materials used on the one hand for the washer and on the other for the tee reactor, in view of the temperatures, pHs and acid concentrations.

Mr. YOUNG : One question concerned the possible hazards with ammonium nitrate mixed with the melts and whether the T.V.A. carried out a specific test to evaluate this. We have not, on this particular product, and up till now made grades containing potash with the ammonium nitrate system. However, over the years T.V.A. has evaluated the sensitivity of fertilisers. We have found that the ammonium phosphate tends to desensitise the system, and our tests generally have shown that, if we have products that contain less than 60% ammonium nitrate together with ammonium phosphate, they did not have a sensitivity hazard. At 60% or higher we would be quite concerned, but at 60% or below we think that the ammonium phosphate actually tends to ameliorate this particular problem. The question was whether the polyphosphate would tend to decrease the sensitivity. We do not, to my knowledge, have any tests that would indicate that particular point.

Mr. NOIRBENT asked why we chose a pug mill for this particular operation, instead of prilling for instance. A pugmill was selected in our early work when we were trying to make products containing 50% or more polyphosphate. In this case a great deal of mechanical working is necessary to induce crystallization and we found that a pug mill or something with positive mixing or mechanical action is helpful. So we followed up with it and we still think it is preferable for some of these grades. Prilling would certainly be practicable and perhaps preferable for the ammonium nitrate type products. With urea prilling would be quite difficult, because mixing of the hot melt with urea, even for a few seconds, gives quite a rapid reaction between the urea and the ammonium phosphate melt to evolve large amounts of CO_2 , and, in a limited test, attempting to mix the urea and melt long enough to prill has been quite difficult. We have had some success in prilling the ammonium phosphate melt alone, but it does not seem to crystallize rapidly enough to be adaptable to air prilling. In summary we think that the product containing ammonium nitrate should prill quite readily and this would probably be the most desirable way. But for the other products we think the blunger still has advantages.

The last question concerned materials of construction and our choice of these materials. We think that selection of the materials of construction is the biggest uncertainty in this process. Because of the high temperature involved, corrosion is a problem essentially throughout the entire system. Our system is made from 316L stainless steel and we have had no severe corrosion problems. However, specimens that have been evaluated and measured for corrosion indicate that stainless steel would not be suitable for some components because of corrosion rates as high as 100 to 500 mills/year. We found that Hastelloy C or Hastelloy G is best for components such as the tee reactor itself. I feel that acid brick lining in the scrubber might be the best choice. We have also investigated teflon lined pipes. The pipeline could be made of teflon lining and the whole system could be brought together quite compactly so that you have very short sections of pipe. And so we think that this would be one of the areas that engineering firms could look into i.e. what would be the best choice of materials and perhaps some actual experience in a large unit will be necessary. We think stainless steel would be suitable in the disengager but more resistant materials would be needed in the scrubber, the tee reactor and the connecting pipe.

Mr. J.D.C. HEMSLEY (Fisons Ltd., U.K.) : My first question relates to the possible difficulties in scaling up the reactor and disengager to full scale. The second question is concerned with the pug mill discharge. Why in your process, do you cool all the material before screening rather than just cool the product after screening ? My third question is whether it is correct to assume that your urea hydrolysis and biuret formation are normally insignificant. My fourth question ; Mr. YOUNG claims that moisture absorption of the bulk product is similar to that of granular diammonium phosphate, suggesting that this is a function of the polyphosphate content. I think it would be useful to have a clear explanation of the mechanism involved here. Fifth question ; the bulk density of the products is given around 0.7 - 0.8 Kg/dm³. My own company's experience in the full scale manufacture of urea ammonium phosphate-based fertilizers is that the bulk density is around 0.9 Kg/dm³. This is an important factor relevant to the economics of storage and distribution. It would therefore be interesting to know why the density of the product made by the T.V.A. pilot-plant appears to be smaller or lower. Finally great advantages are claimed for elimination of the rotary dryer from the process. While it is of course an expensive piece of equipment, it is probably the most reliable and fool-proof item in any granulation plant, with an exceedingly long life. Above all, however, it offers the opportunity for the plant to have the

widest possible flexibility in terms of grade variety. Every fertiliser manufacturer in this room places the highest premium on fertiliser processes which can cope with a wide variety of grades, processes that can cope with year to year developments in product requirements and can do so in the simplest and most unsophisticated equipment. In my view these represent an important limitation to processes such as Mr. YOUNG has described.

Mr. YOUNG : Mr. HEMSLEY's point concerning scale-up of the equipment and what our ideas are : We have gone into this quite thoroughly and we have a tentative scale-up design for a 10t/hour unit. We have certain criteria which we think are established from the pilot-plant work. Scale-up is a considerable concern. However, we have actually had more experience over a long period of time with this system and in changing the mechanical components for dependability, so we feel that scale-up will not be nearly as big a problem as selection of materials of construction.

He mentioned why did we cool all of the material rather than screening hard and cool only the product fraction. This is because we set up this system in an existing pilot-plant and this was the only arrangement we had. For most of these grades, and perhaps all of them, screening hard and decreasing the size of the cooler probably would be practicable and certainly would be preferable, since it would decrease the size of the cooler. We think, in any case, that where you can satisfactorily screen and crush the material hard, that this is a significant advantage.

He mentioned urea hydrolysis and reaction between urea and ammonium phosphate melt, and how we minimize or avoid this in the products. If you recall, in the pug mill we mentioned, it is important to first bring in the recycle and the potassium chloride into the pug mill. Then we spray the urea solution onto the cooler recycle. This allows partial crystallization of the urea and lowers the temperature and so, when the final ammonium phosphate melt is applied, we have a temperature no higher than about 200° F. By following this procedure we have a low enough temperature. When the ammonium phosphate melt contacts the urea the hydrolysis is not rapid. However, we do get some degree of reaction and this is reflected in the bulk density of the products.

Mr. HEMSLEY mentioned that we have had somewhat lower bulk density. We think this is due to at least a minor reaction that gives some evolution of gaseous components and the interior of the granules have been somewhat porous. This has decreased the bulk density. We think all efforts should

be exercised to minimise this reaction and to keep the bulk density as high as would be practical.

Mr. HEMSLEY had some points about elimination of the dryer. I think at least part of them were well taken, in that a dryer does give a great deal of versatility to a process, to allow maximum range of grades and formulations. However, we feel that, for this particular situation, a plant would be designed only for these particular types of grades ; in that situation the elimination of the dryer would be significant. Even if a dryer were installed in the plant, we think there are significant advantages in not operating the dryer because the dryer is one of the main sources of fumes and dust in the fertiliser operation. In our own situation we have a granulation plant, one process has a blunger for ammonium polyphosphate, one has a rotary drum T.V.A. ammoniator for nitric phosphates and a third has a pan granulation system for ammonium phosphate nitrates. In our experience, with the ammonium polyphosphate that does not require a dryer, we have had much less down time and much higher on stream factor than with the other processes. We attribute a large part of that to not having the usual problems in a dryer. However, for maximum versatility of a plant a dryer certainly gives those advantages, as Mr. HEMSLEY pointed out.

Mr. P. MORAILLON (Pechiney-Saint Gobain) : I have several questions.

In the pilot-plant, the pug mill is driven by a 25 H.P. motor. What is the power actually used ? If 54% P_2O_5 phosphoric acid, not pre-heated, is used, what would be the temperature of the acid in the scrubber ? Instead of using Hastelloy G, could one envisage construction of vulcanised steel or lined with carbon bricks ? In spite of its considerable advantages, the process proposed has the disadvantage of fixing less ammonia in the diammonium phosphate - 5.1 to 5.9 lb ammonia per unit of P_2O_5 , as against 9.6 in diammonium phosphate. It is therefore necessary to provide supplementary ammonia as urea, or ammonium nitrate, which are more costly than ammonia. Now, T.V.A. itself has studied, in the laboratory, an ammonium polyphosphate granulation process from slurry. It is the "slurry granulation process" which, in view of the two stage ammoniation of superphosphoric acid by thermic route, would give a 21-55-0 product containing 9.3 lb of ammonia per unit of P_2O_5 . Could one envisage a similar improvement of the process described ?

Mr. YOUNG : Mr. MORAILLON asked a question about the pug mill horsepower. We do have a pug mill with a 25 H.P.

power motor. We are not sure how much is actually used but it is much less than this amount. We usually operate at 30-40% of full loading. However the normal load horsepower is quite high. The pug mill has more power than is needed for this process at the rates of production we used.

He asked a question similar to the one Mr. COATES asked concerning the temperature of acid in the scrubber. The lowest temperature we have used is about 130° C. Here I think that acid resistant or carbon brick lining should be satisfactory. I am not sure what is the upper temperature for rubber lining but I think this would be beyond the range for rubber lining.

He mentioned a very important point concerning the fact that, in this process, we fix ammonia only slightly above monoammonium phosphate and pointed out that, in products where we make diammonium phosphate, almost twice that amount of ammonia is incorporated. This is an economic advantage in most cases because ammonia is usually the cheapest source of nitrogen. So, since these products have less ammonia in them, more of the final nitrogen comes from urea and, in the final products the nitrogen would be somewhat more expensive in this system than it would in a diammonium phosphate system. However, we see other advantages that we think would tend to offset that cost.

He mentioned another process which is undergoing laboratory studies at T.V.A. - a two step process for crystallizing a polyphosphate material. This is different from this process but these studies are continuing and we perhaps will be going into these studies on a pilot-plant scale before too long. The laboratory work has indicated that this two step process could be used for either furnace acid or wet process acid, but the process is so different from the melt process that we see no application of these particular principles in this melt process.

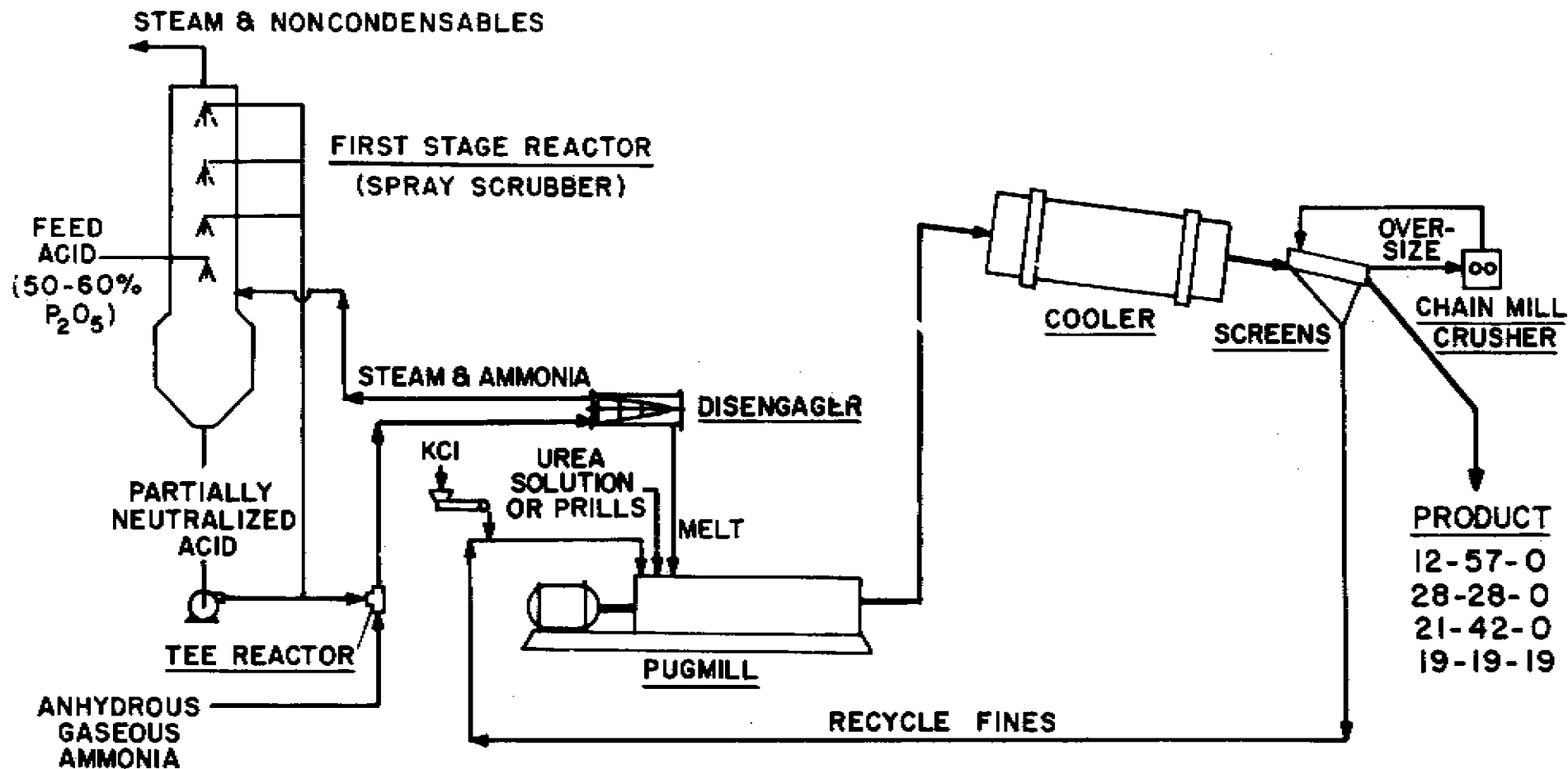


FIGURE 1

Flow Diagram for Direct Production of Low - Polyphosphate Granular Products

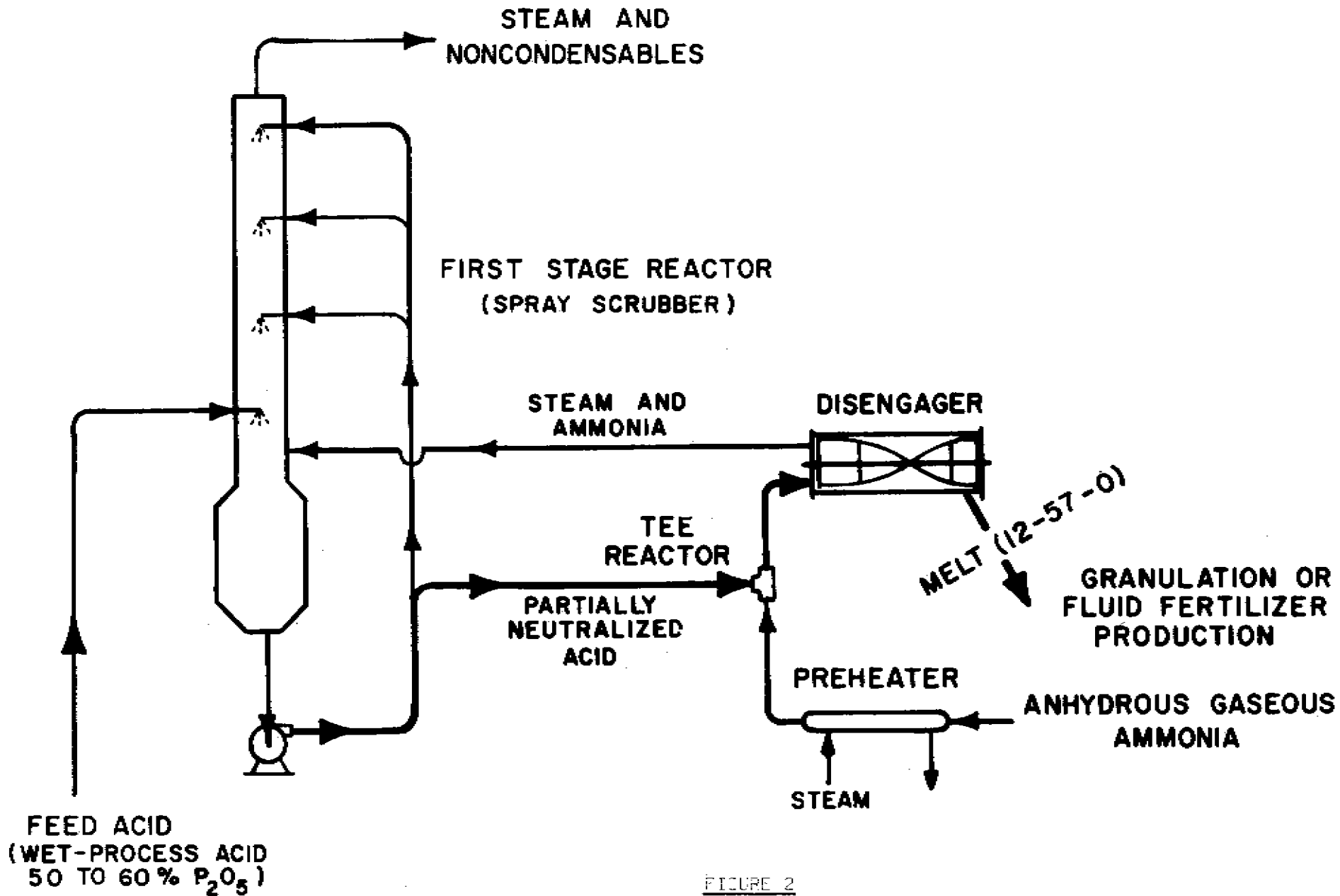


FIGURE 2

Flow Diagram of Reaction System for Direct Production of Ammonium Polyphosphate

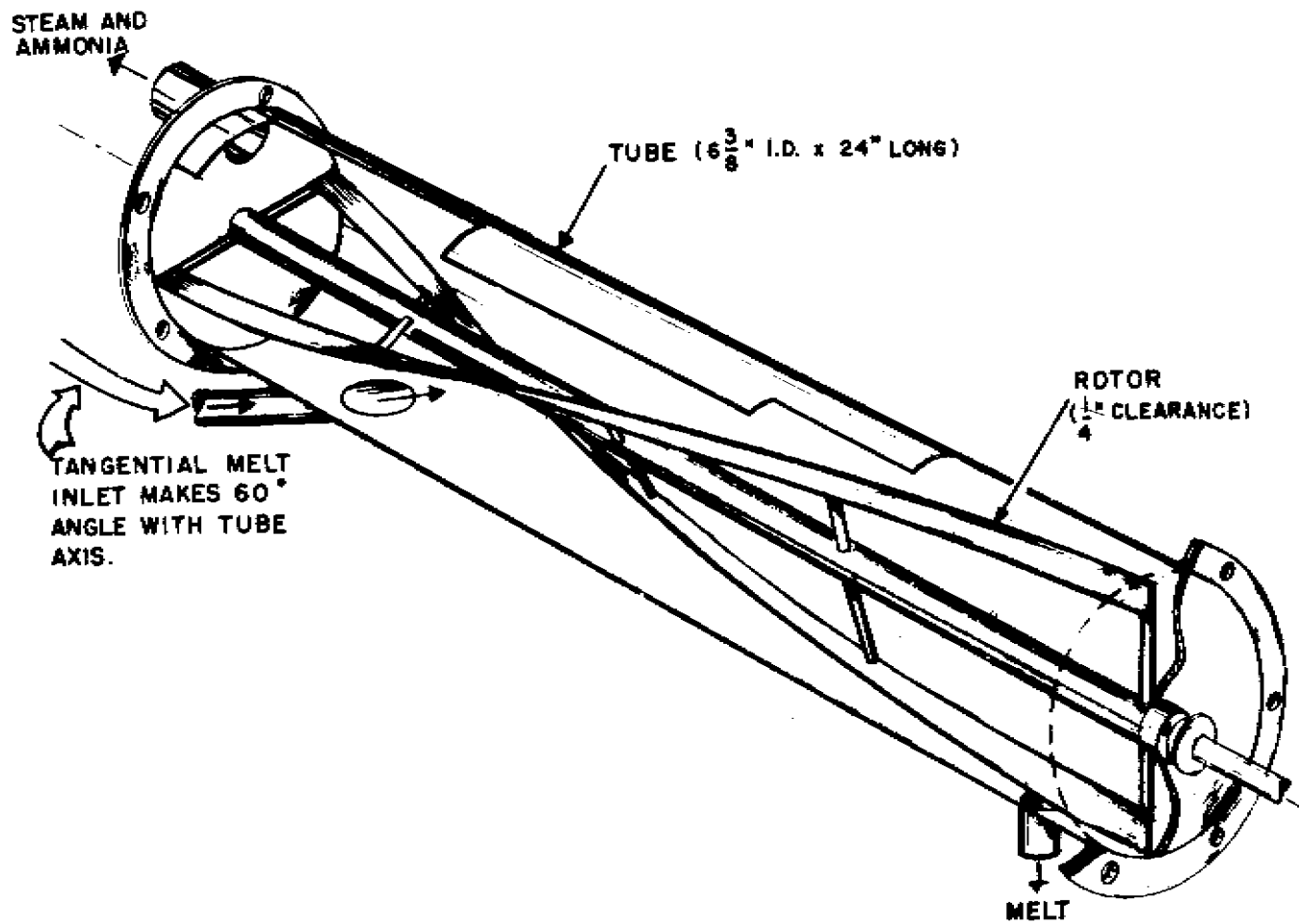


FIGURE 3

Vapor Disengager

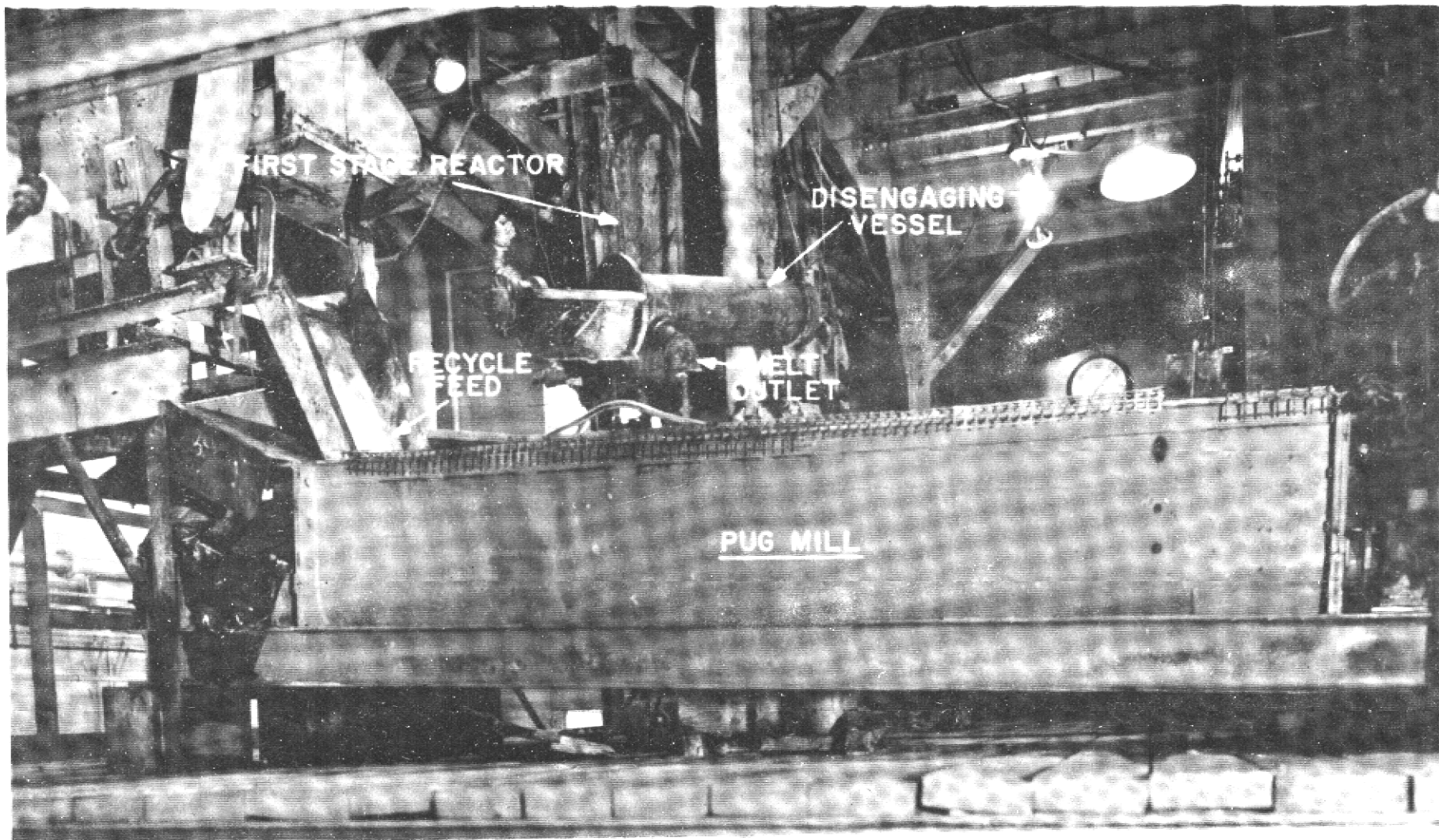


FIGURE 4

Equipment Arrangement for Production
of Granular Products

Appareillage pour la production
d'engrais granulés